

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
11 April 2002 (11.04.2002)

PCT

(10) International Publication Number
WO 02/28965 A1

(51) International Patent Classification⁷: C08L 53/02, C08F 297/04

(21) International Application Number: PCT/US01/31134

(22) International Filing Date: 4 October 2001 (04.10.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/237,533 4 October 2000 (04.10.2000) US

(71) Applicant (for all designated States except US): KRA-
TON POLYMERS RESEARCH, B.V. [NL/NL]; P.O.
Box 37666, NL-1030 BH Amsterdam (NL).

(72) Inventors; and

(75) Inventors/Applicants (for US only): DJIAUW, Lie,
Khong [US/US]; 15959 Sogma Creek Drive, Houston,
TX 77095 (US). HANDLIN, Dale, Lee, Jr. [US/US];
2816 Windchase Boulevard, Houston, TX 77082 (US).
MODIC, Michael, John [US/US]; 1607 Pecan Crossing,
Richmond, TX 77469 (US).

(74) Agent: TACKETT, Keith, M.; Moser, Patterson & Sheri-
dan, LLP, Suite 1500, 3040 Post Oak Boulevard, Houston,
TX 77056 (US).

(81) Designated States (national): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI,
SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU,
ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,
IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF,
CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD,
TG).

Declaration under Rule 4.17:

— of inventorship (Rule 4.17(iv)) for US only

Published:

— with international search report
— before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.



WO 02/28965 A1

(54) Title: AN ELASTOMERIC FILM AND FIBER GRADE THERMOPLASTIC ELASTOMER COMPOSITION

(57) Abstract: In one embodiment, the present invention provides an elastomeric composition which is useful as an elastic film and fiber grade compound. These compositions contain at least one SEBS block copolymer having a vinyl content of 60 percent or greater and a molecular weight of 40,000 to 110,000 and a styrene block molecular weight of 5,000 to 15,000. The composition will comprise from 60 to 85 percent by weight of the block copolymer, from 5 to 25 percent by weight of a tackifying resin, and from 5 to 35 percent by weight of a low molecular weight, low density polyethylene. In a second embodiment of the present invention, an elastic film and fiber grade compound is provided which does not contain a tackifying resin. The composition is comprised of from 15 to 30 percent by weight of a low molecular weight, low density polyethylene and the balance is comprised of the block copolymer described above. A third embodiment of this invention provides another elastic film and fiber grade compound. This compound also contains no tackifying resin. It is comprised of from 2 to 60 percent by weight of a metallocene polyethylene elastomer polymer and the balance is the block copolymer described above.

AN ELASTOMERIC FILM AND FIBER GRADE THERMOPLASTIC ELASTOMER COMPOSITION

5 CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims benefit of United States provisional patent application serial number 60/237,533, filed October 4, 2000, which is herein incorporated by reference.

10 FIELD OF THE INVENTION

This invention relates to elastomeric polymer compositions that can be extruded into fibers or films. More specifically, the invention relates to new high vinyl styrene-diene block copolymer compositions for use in making film or spun bond fiber for elastic nonwovens laminates.

15 BACKGROUND OF THE INVENTION

Extrudable elastomeric compositions which can be easily compression molded or melt blown into elastic fibers or films having low stress relaxation, low hysteresis, and high recoverable energy are known. The elastomeric fibers or films are useful in making a variety of applications such as diaper waistbands and non-woven
20 fabrics.

A number of thermoplastic elastomer compositions have been developed for making film or spun bond fiber nonwovens laminate for personal hygiene applications. U.S. Patent 4,789,699 disclosed such compositions based on styrene-ethylene/butylene-styrene (SEBS) polymers the incorporate additional tackifier and
25 polyolefin resins. One of the drawbacks of this composition was the relatively poor elastic recovery performance. U.S. Patent No. 5,093,422 discloses composition based on styrene-propylene/ethylene styrene (SEPS) polymers which are said to improve the elastic properties of the materials. However, the flow behavior of these compositions was reduced. U.S. Patent No. 5,332,613 discloses a composition
30 based on styrene-ethylene/propylene-styrene-ethylene/propylene (SEPSep) four-block polymers as a way to balance the hysteresis and flow performance. However, none of the above technologies provide a desirable balance of important properties:

elastic hysteresis, stress relaxation at body temperature and ease of flow characteristics. The stress relaxation at body temperature tends to be the most critical shortcoming in these compositions.

SEBS elastomeric block copolymers and SEPS elastomeric block copolymers
5 have been blended as discussed above to form extrudable elastomeric compositions which can be formed into elastic fibers or films. While the additives, tackifying resins or polyolefins, improve the extrusion properties of the compositions and the processing and/or bonding properties of the elastic fibers or films, such additives have an adverse affect on the elastic properties of the resulting fiber or film,
10 especially at temperatures above 25°C.

It can be seen that it would be advantageous to provide an elastomeric composition which overcomes the drawbacks of the above prior art compositions. An elastomeric composition which maintained or improved the elastic performance of the products made therefrom and which also exhibits improved flow behavior
15 which is highly desirable in film and fibers applications would be particularly advantages. The present invention provides such an elastomeric composition.

SUMMARY OF THE INVENTION

In one embodiment, the present invention provides an elastomeric composition which is useful as an elastic film and fiber grade compound. These compositions
20 contain at least one SEBS block copolymer having a vinyl content of 60 percent or greater and a number average molecular weight of 40,000 to 110,000, preferably 60,000 to 100,000, and a styrene block molecular number average weight of 5,000 to 15,000. The composition will comprise from 60 to 85 percent by weight of the block copolymer, from 5 to 25 percent by weight of a tackifying resin, and from 10 to
25 35 percent by weight of a polyethylene.

In a second embodiment of the present invention, an elastic film grade compound is provided which does not contain a tackifying resin. The composition is comprised of from 5 to 35 percent by weight of a polyethylene and the balance is comprised of the block copolymer described above.

30 A third embodiment of this invention provides another elastic film grade compound. This compound also contains no tackifying resin. It is comprised of from

2 to 60 percent by weight of a metallocene polyethylene elastomer polymer and the balance is the block copolymer described above.

The term "vinyl content" refers to the fact that a conjugated diene is polymerized via 1,2-addition (in the case of butadiene - it would be 3,4-addition in the case of isoprene). Although a pure "vinyl" group is formed only in the case of 1,2-addition
5 polymerization of 1,3-butadiene, the effects of 3,4-addition polymerization of isoprene (and similar addition for other conjugated dienes) on the final properties of the block copolymer will be similar. The term "vinyl" refers to the presence of a pendant vinyl group on the polymer chain.

10 **DETAILED DESCRIPTION OF THE INVENTION**

The extrudable elastomeric composition of the present invention is an improvement of the extrudable compositions described in United States Patents Nos. 4,970,259, 5,093,422, and 5,332,613 which descriptions are incorporated by reference herein. The known compositions include one or more styrenic block
15 copolymers, typically an SEBS or an SEPS or an SEPSep elastomeric block copolymer which is produced by hydrogenating a polystyrene-polybutadiene-polystyrene or polystyrene-polyisoprene-polystyrene or polystyrene-polyisoprene-polystyrene block copolymer. The SEBS block copolymers which were specifically discussed and utilized in the above patents all had vinyl contents in the
20 "normal" range of 35 to 55 percent by weight.

In the present invention, the compositions contain at least one hydrogenated polystyrene-polybutadiene-polystyrene block copolymer (S-EB-S) having a vinyl content in the saturated block of polybutadiene of at least 60 percent by weight and preferably from 60 to 85 percent by weight in comparison to the conventional block
25 copolymers used to make elastomeric films and fibers commercially and described in the above patents. This change in microstructure results in improved elastic performance and flow behavior while maintaining the stress relaxation properties of the conventional block copolymers. The S-EB-S block copolymer may be blended with other hydrogenated block copolymers, such as the SEPS or the SEPSep
30 elastomeric block copolymers, or the butadiene may be co-polymerized with other conjugated dienes, such as isoprene, in amounts that retain improved elastomeric properties.

The styrenic block copolymers have at least two poly(monoalkenylarene) blocks, preferably two polystyrene blocks, separated by a saturated block of a poly(conjugated diene), preferably a saturated polybutadiene. The preferred block copolymers comprise two polystyrene blocks, at least one block having a number
5 average molecular weight from 5,000 to 15,000, and one saturated polybutadiene midblock, each having a number average molecular weight from 30,000 to 85,000. The saturated polybutadiene blocks preferably have at least 60 percent by weight 1,2-configuration (vinyl content) and preferably from 60 to 85 percent. The total number average molecular weight of the block polymer is from 40,000 to 110,000,
10 preferably 60,000 to 100,000, and the block copolymers preferably have an average polystyrene content from 12% to 25% by weight.

These polymers may be prepared using free-radical, cationic and anionic initiators or polymerization catalysts. Such polymers may be prepared using bulk, solution or emulsion techniques. In any case, the polymer containing at least
15 ethylenic unsaturation will, generally, be recovered as a solid such as a crumb, a powder, a pellet, or the like.

In general, when solution anionic techniques are used, conjugated diolefin polymers and copolymers of conjugated diolefins and alkenyl aromatic hydrocarbons are prepared by contacting the monomer or monomers to be polymerized
20 simultaneously or sequentially with an organoalkali metal compound in a suitable solvent at a temperature within the range from about -150°C to about 300°C, preferably at a temperature within the range from about 0°C to about 100°C. Particularly effective anionic polymerization initiators are organolithium compounds having the general formula:

25
$$RLi_n$$

wherein R is an aliphatic, cycloaliphatic, aromatic, or alkyl-substituted aromatic hydrocarbon radical having from 1 to about 20 carbon atoms; and n is an integer of 1 to 4.

In addition to sequential techniques to obtain triblocks, tetrablocks, and higher
30 orders of repeating structures, anionic initiators can be used to prepare diblocks of polystyrene-polydiene having a reactive ("live") chain end on the diene block which

can be reacted through a coupling agent to create, for example, (S-I)_xY or (S-B)_xY structures wherein x is an integer from 2 to about 30, Y is a coupling agent, I is isoprene, B is butadiene and greater than 65 percent of S-I or S-B diblocks are chemically attached to the coupling agent. Y usually has a molecular weight which is low compared to the polymers being prepared and can be any of a number of materials known in the art, including halogenated organic compounds; halogenated alkyl silanes; alkoxy silanes; various esters such as alkyl and aryl benzoates, difunctional aliphatic esters such as dialkyl adipates and the like; polyfunctional agents such as divinyl benzene (DVB) and low molecular weight polymers of DVB. Depending on the selected coupling agent the final polymer can be a fully or partially coupled linear triblock polymer (x=2), i.e., SIYIS; or branched, radial or star configurations. The coupling agent, being of low molecular weight, does not materially affect the properties of the final polymer. DVB oligomer is commonly used to create star polymers, wherein the number of diene arms can be 7 to 20 or even higher.

The styrenic block copolymers must be hydrogenated. In general, the hydrogenation or selective hydrogenation of the polymer may be accomplished using any of the several hydrogenation processes known in the prior art. For example the hydrogenation may be accomplished using methods such as those taught, for example, in U.S. Patent Nos. 3,494,942; 3,634,594; 3,670,054; 3,700,633; and Re. 27,145, the disclosure of which patents are incorporated herein by reference. The methods known in the prior art and useful in the present invention for hydrogenating polymers containing ethylenic unsaturation and for hydrogenating or selectively hydrogenating polymers containing aromatic and ethylenic unsaturation, involve the use of a suitable catalyst, particularly a catalyst or catalyst precursor comprising an iron group metal atom, particularly nickel or titanium or cobalt, and a suitable reducing agent such as an aluminum alkyl. The amount of ethylenic unsaturation remaining after hydrogenation is typically less than 20%. The level of saturation achieved by hydrogenation is desirably greater than about 95%. For example, the level of saturation achieved by hydrogenation is desirably greater than about 98%. More desirably, the level of saturation achieved by hydrogenation is greater than about 99%.

In general, the hydrogenation will be accomplished in a suitable solvent at a temperature within the range from about 20°C to about 100°C and at a hydrogen partial pressure within the range from about 100 psig (8 bar) to about 5,000 psig (350 bar), preferably about 100 psig (8 bar) to 1,000 psig (70 bar). Catalyst concentrations within the range from about 10 ppm (wt) to about 500 ppm (wt) of metal based on total solution are generally used and contacting at hydrogenation conditions is generally continued for a period of time within the range from about 60 to about 240 minutes. After the hydrogenation is completed, the hydrogenation catalyst and catalyst residue will, generally, be separated from the polymer.

The compositions of the present invention may include from 5 to 35 percent by weight of one or more polyolefins. The polyolefins which may be utilized in the extrudable composition must be polyolefins which, when blended with the elastomeric block copolymer or a mixture of elastomeric block copolymers and subjected to an appropriate combination of elevated pressure and elevated temperature conditions, is extrudable, in blended form, with the elastomeric block copolymer or a mixture of elastomeric block copolymers. In particular, preferred polyolefin materials include low molecular weight low density polyethylene with a density of less than 0.92 grams per cubic centimeter and a melt index greater than 30 grams/10 minutes, and linear low density polyethylene, metallocene linear low density polyethylene, various ethylene copolymers, such as low vinyl acetate polyethylene, ethylene methyl acrylate copolymer, ethylene acrylic acid, ethylene methacrylic acid resins etc. Blends of two or more of the polyolefins may be utilized.

An example of a low molecular weight, low density polyethylene is Petrothene NA 601-04 (also referred to herein as PE NA 601) obtained from Equistar Chemical. Information obtained from Equistar Chemical states that PE NA 601 is a low molecular weight, low density polyethylene for application in the areas of hot melt adhesives and coatings. PE NA 601 exhibits following key characteristics: (1) a density of 0.903 grams per cubic centimeter when measured in accordance with ASTM D 1505; and (2) an equivalent Melt index of 2,000 grams per 10 minutes when measured in accordance with ASTM D 1238.

In another embodiment of this invention, the above block copolymers are blended with a metallocene polyolefin having a density from 0.86 to 0.91, a

molecular weight distribution less than 3, and from 8% to 30% by weight of an α -olefin comonomer having from 4 to 12 carbon atoms, preferably from 4 to 8 carbon atoms. The metallocene polyolefins are polyolefins produced with a metallocene catalyst as described in United States Patents No. 5,322,728 and 5,272,236 which
5 are descriptions are incorporated by reference herein. Such elastomeric polyolefins are available from DuPont Dow Elastomers under the trademark ENGAGE (ethylene/octene copolymers), from Dow Chemical Company under trademark AFFINITY, and from Exxon Chemical Company under the trademark EXACT (ethylene/butene copolymers). The metallocene polyolefins have low crystallinity
10 when ethylene is copolymerized with from 8% to 30% by weight of an α -olefin comonomer having from 4 to 12 carbon atoms.

Various tackifying resins can be used in at least one of the embodiments of the present invention. In particular, the purpose of the tackifying resin is to allow elastomeric film or fiber to act as a pressure sensitive adhesive, e.g., to allow
15 elastomeric film or fiber to bond to another web or layer of material. Of course, various tackifying resins are known, and are discussed, e.g., in U.S. Patent Nos. 4,789,699; 4,294,936; and 3,783,072, the contents of which, with respect to the tackifier resins, are incorporated herein by reference. Any tackifier resin can be used which is compatible with the elastomeric polymer and the polyolefin, and can
20 withstand the high processing (e.g., extrusion) temperatures. Generally, hydrogenated hydrocarbon resins are preferred tackifying resins, because of their better temperature stability. The following paragraphs disclose information on three specific tackifying resins, two of which (REGALREZ® and ARKON®P series tackifiers) are examples of hydrogenated hydrocarbon resins, and the
25 ZONATAC®501 Lite is a terpene hydrocarbon. Of course, while the three tackifying resins are specifically discussed, the present invention is not limited to use of such three tackifying resins, and other tackifying resins which are compatible with the other components of the composition and can withstand the high processing temperatures, and can achieve the objectives of the present invention, can also be
30 used.

REGALREZ® hydrocarbon resins, a product of Hercules, Incorporated, are fully hydrogenated α -methylstyrene, low molecular weight hydrocarbon resins, produced by polymerization and hydrogenation of pure monomer hydrocarbon feed stocks.

Grades 1094, 3102, 6108, and 1126 are highly stable, light-colored low molecular weight, nonpolar resins suggested for use in plastics modification, adhesives, coatings, sealants, and caulks. The resins are compatible with a wide variety of oils, waxes, alkyds, plastics, and elastomers and are soluble in common organic solvents.

ZONATAC®501 Lite resin, a product of Arizona Chemical Co., has a softening point of 105°C, a Gardner color (50% in heptane) of 1—and a Gardner color neat (pure) of 2+; (a Gardner color of 1—(50% in heptane) is approximately equal to APHA color = 70) a specific gravity (25°/25°C) of 1.02 and a flash point (closed cup, °F) of 480°F.

In one embodiment of the present invention, a composition according to the present invention is provided as an elastic fiber grade compound. This composition comprises from 60 to 85 percent by weight of the above-described high vinyl content block copolymer, from 5 to 25 percent by weight of one of the above-described tackifying resins, and from 10 to 35 percent by weight of one of the above-described polyethylene resin. These compounds show excellent hysteresis recovery and good stress relaxation properties at body temperature. Increasing the vinyl content improves both of these properties as compared to the same polymer with a lower vinyl content. Additionally, these compounds exhibit improved melt flow characteristics and elasticity over compounds comprising similar polymers with lower vinyl contents.

In another embodiment of the present invention, a composition is provided which is a low molecular weight, low density polyethylene containing film compound. This compound does not contain any tackifying resin in order to minimize the softening effect of the tackifying resin. It will comprise from 15 to 35 percent of the low molecular weight, low density polyethylene material described above and the balance will be comprised of the high vinyl block copolymer described above. Within this composition range, these compounds exhibit improved elastic behavior and improved melt flow compared to compounds made from a similar polymer with a lower vinyl content. If the amounts of low molecular weight, low density polyethylene is increased to 50 percent, the compatibility of the high vinyl block

copolymer and the polyethylene is poor. Also, such compounds exhibit poor tensile elongation and cannot sustain the stress relaxation test.

In a third embodiment of this invention, another film grade compound is provided. This compound also contains no tackifying resin and it contains a
5 metalocene elastomer polymer which is used instead of the low molecular weight, low density polyethylene or the combination of tw. This composition will contain from 2 to 60 percent by weight of the metalocene polyolefin and the balance is comprised of the high vinyl block copolymer described above. The compatibility of these polymers within this composition range is good. The blends are
10 homogeneous and they exhibit excellent elastic properties even at the 50/50 blend ratio.

While the principal components of the extrudable elastomeric composition used to form the elastic sheet have been described in the foregoing, such extrudable elastomeric composition is not limited thereto, and can include other components
15 not adversely affecting the extrudable elastomeric composition attaining the stated objectives. Exemplary materials which could be used as additional components would include, without limitation, pigments, antioxidants, stabilizers, surfactants, waxes, flow promoters, solvents, particulates, and materials added to enhance processability and pellet handling of the composition.

The term "elastic" is used herein to mean any material which, upon application
20 of a biasing force, is stretchable, that is, elongatable at least about 60 percent (i.e., to a stretched, biased length which is at least about 160 percent of its relaxed unbiased length) and which, will recover at least 55 percent of its elongation upon release of the stretching, elongating force. A hypothetical example would be a one
25 (1) inch sample of a material which is elongatable to at least 1.60 inches (4.06 cm) and which, upon being elongated to 1.60 inches (4.06 cm) and released, will recover to a length of not more than 1.27 inches (3.23 cm). Many elastic materials may be elongated by much more than 60 percent (i.e., much more than 160 percent of their relaxed length), for example, elongated 100 percent or more, and many of these will
30 recover to substantially their initial relaxed length, for example, to within 105 percent of their initial relaxed length, upon release of the stretching force.

As used herein, the term "stress relaxation" refers to the percent loss of tension or load between the maximum load or force encountered after elongating an elastic material at a specified rate of extension to a predetermined length (or the load or force measured at some initial length) and the remaining load or force measured after the sample has been held at that length for a specified period of time, for example, from about 10 minutes to about 30 minutes. Except where otherwise noted for the present invention, stress relaxation is expressed as a percentage loss of the initial load encountered at a specified extension of an elastic material. The stress relaxation is determined by calculating the difference between the initial maximum load measured after elongating an elastic material at a rate of 20 inches (50.8 cm) per minute to an elongation of 160 percent (i.e., to 260 percent of the material's initial length) and the remaining load measured after that sample was held at that length for 30 minutes divided by the initial maximum load at that length. Testing may be performed on an Instron Model 5565 Universal Test Machine using ASTM microtensile specimens. Stress relaxation after 30 minutes at, for example, an elongation of 160 percent (i.e., to 260 percent of the material's initial length - from 100 mm to 260 mm) may be expressed as a percentage utilizing the following equation: stress relaxation = $(\text{peak load}_{160\%} - \text{load}_{160\% @ 30 \text{ min}}) / (\text{peak load}_{160\%}) * 100$.

As used herein, the term "tensile strength" refers to the resistance of an elastic material to being elongated as determined in accordance with ASTM 412 Method using microtensile specimens that are cut from films. Films formed from a blend of an elastomeric block copolymer and other materials such as, for example, a polyolefin (metallocene and/or crystalline), a tackifier, and/or an extending oil were compression molded. Tensile testing may be performed on an Instron Model 5565 Universal Test Machine.

As used herein, the term "recoverable energy" refers to the energy stored by an elastic material when it is elongated to a specified length. Recoverable energy is measured utilizing a tensile testing apparatus such as, for example, an Instron Model 5565 Universal Test Machine by elongating a sample of an elastic material sample at 1 inch/minute to 150 percent elongation (i.e., to 250 percent of the material's initial relaxed length) and cycling back to zero load for 1 hysteresis loop. The percent recoverable energy is determined by dividing the area under the

retraction curve of the first hysteresis loop by the area under the elongation curve of the first hysteresis loop and then multiplying by 100.

As used herein, the "number average molecular weight" was determined utilizing gel permeation chromatography techniques for linear anionic polymers. All molecular weights are measured prior to hydrogenation which will increase the molecular weights by a small amount. The molecular weights of linear polymers or unassembled linear segments of polymers such as mono-, di-, triblock, etc., arms of star polymers before coupling are conveniently measured by Gel Permeation Chromatography (GPC), where the GPC system has been appropriately calibrated. For anionically polymerized linear polymers, the polymer is essentially monodisperse (weight average molecular weight/number average molecular weight ratio approaches unity), and it is both convenient and adequately descriptive to report the "peak" molecular weight of the narrow molecular weight distribution observed. Usually, the peak value is between the number and the weight average. The peak molecular weight is the molecular weight of the main species shown on the chromatograph. For polydisperse polymers the weight average molecular weight should be calculated from the chromatograph and used. For materials to be used in the columns of the GPC, styrene-divinyl benzene gels or silica gels are commonly used and are excellent materials. Tetrahydrofuran is an excellent solvent for polymers of the type described herein. A refractive index detector may be used.

EXAMPLES

SEBS block copolymers of varying 1,2-vinyl content were made for these experiments. The conventional SEBS polymers of standard vinyl content (38 to 45 percent) were synthesized with diethylether as the structure modifier. The higher vinyl content polymers were synthesized with 1,2-diethoxy propane as the structure modifier. The first group of polymers, which are described in Table I, consists of SEBS polymers with about 100,000 overall total number average molecular weight, 13 to 21 percent polystyrene content, and vinyl contents ranging from 38 to 78 percent. The referenced conventional SEBS polymer (vinyl content of 38 percent) is typically used in high performance elastic SEBS polymer blends for film and fibers applications.

The compound samples were prepared by melt blending the raw ingredients in a small Brabender Kneader at 400°F (204°C). Test samples were compression molded into 25 mil, 4 in. (10.2 cm) by 4 in. (10.2 cm) rectangular plaques at 380°F (193°C). ASTM micro tensile test specimens were die cut from the test plaques.

5 The stress-strain properties of the pressed films were determined in accordance with ASTM D-412 utilizing a Constant Rate of Extension Tester, Instron Model 5565 Universal Testing Instrument. Each sample was placed lengthwise in jaw faces, with a jaw span of 0.75 inches (1.9 cm). The Instron Model 5565 Universal Test Instrument crosshead speed was set at 2 inches per minute for the
10 first series of tests measuring the Stress-Strain properties. In addition, stress relaxation and hysteresis tests were measured using the Instron Model 5565 Universal Test Machine and determined as previously described. The specimens were cut orthogonally and the results were reported based on the average of both directions.

15 Table I lists the characteristics and physical properties of the three polymers which were used to make the compounds which are evaluated in Tables II and III. It can be seen that the melt flow of the higher vinyl polymers is significantly higher than that of the standard vinyl content SEBS block copolymer and the rubber moduli of the higher vinyl polymers are lower than the referenced polymer (Polymer A).
20 The elastic recovery behavior of the higher vinyl polymers is significantly better than the reference polymer while their stress relaxation properties at body temperature remain unchanged.

Example 1

Elastic fiber grade compounds containing the SEBS polymers of Table I were
25 made and their corresponding physical properties are shown in Table II. Two types of elastic film formulations were used in this example. The first type of formulation (compounds 1, 2 and 3 in Example 1, Table II) contains SEBS block copolymer, tackifying resin, and a low density polyethylene resin. The polyethylene resin used was Equistar NA 601-04 which is described in detail above. This type of compound
30 also exhibits hot melt adhesive behavior with the plasticization of the midblock by the tackifying resin. These compounds show excellent hysteresis recovery and

good stress relaxation properties at body temperature. Increasing the vinyl content in the midblock improves both the hysteresis recovery and the stress relaxation. Of most interest is the improvement of stress relaxation of the high vinyl polymer compounds at body temperature. Elastic recovery and stress relaxation behavior of the compounds made from the high vinyl SEBS block copolymers B and C are the best among these compounds and thus compounds 2 and 3 with their improved melt flow and elasticity are preferred.

Table I

Polymer Number	A	B	C
Characterizations			
1,2 Vinyl Content, % by weight	37.5	60.6	78
Block Molecular Weight by GPC	6.9-82.5-8.4	7.5-83.6-9.4	9/8-80-12.6
Hydrogenated Total Molecular Weight	97,000	100,000	103,600
Polystyrene Content, % by weight	12.8	15	20.6
Properties of Polymer			
Melt Flow @ 230°C/5.0 Kg. grams/10 min.	<1.0	5.3	4.25
Mechanical Properties at 23°C			
Stress Relax., % 30 min., 160%	17	17	20
Stress Strain Properties			
100% modulus, psi (Kg/cm ²)	226 (15.9)	150 (10.5)	176 (12.4)
300% modulus, psi (Kg/cm ²)	370 (26.0)	230 (16.2)	307 (21.6)
500% modulus, psi (Kg/cm ²)	627 (44.1)	345 (24.3)	448 (31.5)
Tensile Strength, psi (Kg/cm ²)	1556 (109)	1230 (86.5)	* >1233 (>86)
Elongation at Break, psi (Kg/cm ²)	787 (55.3)	1070 (75.2)	* >1114 (>78)
Hysteresis to 150%			
Hysteresis to 150% elongation	246	170	235
% Recovery	77.5	88	80.3
% Set	11	12	10
Stress Relaxation at 40°C			
% Stress Relax., 30 min., to 160% extension	24	23	22

* No break

Example 2

The second type of compounds described in Table II are binary blends of SEBS block copolymer and the same low density polyethylene resin used above.

The compounds were prepared with SEBS/PE blend ratios of 85/15, 70/30, and 50/50 levels. The results are shown in Table II (Example 2, compounds 4 to 16). At blend ratios between 85/15 and 70/30, the high vinyl polymer compounds exhibit improved elastic behavior and improved melt flow compared to compounds from the reference polymer. The compatibility of the high vinyl SEBS polymer with low molecular weight, low density polyethylene is poor at the higher polyethylene content. Also, the 50/50 blend exhibited poor tensile elongation and could not sustain the stress relaxation test.

Example 3

10

Several film grade compounds utilizing a metallocene polyethylene elastomer were made. The particular metallocene was Dow Affinity® resin having a density of 0.885 and a melt index of 30. The compatibility of this metallocene polymer with the high vinyl SEBS polymers is good. The blends appear homogeneous and exhibit excellent elastic properties at a 50/50 blend ratio. Table III shows the comparison of physical properties of blends of polymer A,B and C with low density polyethylene and metallocene linear low density polyethylene at 30 and 50% polyethylene level.

The blends of high vinyl polymers B and C, formulation 12, 13, 17 and 18, exhibit better flow than formulations 7 and 8 made with "normal" vinyl polymer A while maintaining equivalent or better recoverable energy, permanent set and stress relaxation.

20

Table II

Formulation	Example 1					Example 2									
	-1	-2	-3	-4	-5	-6	-9	-10	-11	-14	-15	-16			
Composition, % wt															
Polymer A, 38% vinyl SEBS	67.8			84.8	69.8	49.8									
Polymer B, 60% vinyl SEBS		67.8					84.8	69.8	49.8						
Polymer C, 78% vinyl SEBS			67.8							84.8	69.8	49.8			
Regalrez 1126	20	20	20												
PE, NA601-04	12	12	12	15	30	50	15	30	50	15	30	50			
AO 330	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2			
Total, % wt	100	100	100	100	100	100	100	100	100	100	100	100			
Properties of Compound															
Melt Flow @ 190°C/2.16 Kg. grams/10 min.	<1.0	3.12	1.23	<1.0	<1.0	4.7	<1.0	4.34	>20	<1.0	4.69	>20			
Mechanical Properties at 23°C, % Stress Relax, 160 % 30 min.	22.7	20.9	24.6	22.9	27.4	37.2	17.8	26.8	38.5	23.9	31.9	Sample Broke			
Stress Strain Properties															
100% modulus, Kg/cm ²	14.1	8.86	6.40	18.7	21.9	31.1	13.0	17.8	27.1	11.7	17.0	23.4			
300% modulus, Kg/cm ²	21.0	14.1	10.9	29.0	32.0	41.7	19.9	26.8	33.4	20.7	25.3	-			
500% modulus, Kg/cm ²	32.3	21.0	16.5	46.5	49.6	58.0	29.2	36.6	-	30.0	34.1	-			
Tensile Strength, Kg/cm ²	97.7	>69.7	>51.7	125.6	135.9	79.2	>102	72.0	35.7	81.2	51.4	24.2			
Elongation at Break, Kg/cm ²	65.3	>78.7	>78.7	62.8	64.8	46.6	>78.8	61.8	28.5	78.2	66.5	12.4			
Hysteresis to 150% extension															
Peak Stress, Kg/cm ²	15.3	10.2	7.5	21.6	23.8	32.8	14.8	20.2	28.6	14.3	19.0	Broke			
% Recovery	71	82	80	70	62	42	82	67	42	76	55	-			
% Set	10.8	12.1	11.9	15.7	17.7	28	11.9	15.6	27.1	12.3	19.3	-			
Properties at 40°C															
% Stress Relax, 160% extension for 30 min.	44	35.9	26.4	31.1	33.2	48.5	31.1	36	Broke	25.2	Broke	Broke			

Note: " > " symbol indicates sample did not break at that elongation.

Table III

Formulation	-5	-6	-7	-8	-10	-11	-12	-13	-15	-16	-17	-18
Composition, % wt												
Polymer A, 38% vinyl SEBS	69.8	49.8	69.8	49.8								
Polymer B, 60% vinyl SEBS					69.8	49.8	69.8	49.8				
Polymer C, 78% vinyl SEBS									69.8	49.8	69.8	49.8
PE, NA601-04	30	50			30	50			30	50		
AFFINITY® Resin, 30 MI			30	50			30	50			30	50
AO 330	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Total, % wt	100	100	100	100	100	100	100	100	100	100	100	100
Properties of Compound												
Melt Flow @ 190°C/2.16 Kg, grams/10 min.	<1.0	4.66	<1.0	1	4.34	>20	<1.0	4.04	4.69	>20	<1.0	2.34
Mechanical Properties at 23°C.												
% Stress Relax., 160 % extension for 30 min.	27.4	37.2	25.8	28.6	26.8	38.5	23.8	29.1	31.9	Broke	25.5	30.7
Stress Strain Properties												
100% modulus, Kg/cm ²	21.9	31.1	20.3	24.2	17.8	27.1	16.5	22.6	17.0	23.4	16.7	20.8
300% modulus, Kg/cm ²	32.0	41.7	30.8	35.5	26.8	33.4	25.0	31.5	25.3	-	25.9	30.4
500% modulus, Kg/cm ²	49.6	58.0	47.1	51.2	36.6	-	34.9	41.9	34.1	-	35.7	40.1
Tensile Strength, Kg/cm ²	135.9	79.2	123.7	123.1	72.0	A	>112	106.0	51.4	A	>91	>92.1
Elongation at Break, Kg/cm ²	64.8	46.6	64.6	64.5	61.8	< 35.2	>78.7	76.1	66.5	< 21.1	>77.8	>
Hysteresis to 150%												
Peak Stress, Kg/cm ²	23.8	32.8	22.3	26.9	20.2	28.6	18.5	24.0	19.0	-	18.6	23.6
% Recovery	62	42	67	57	67	42	73	59	55	-	68	56
% Set	17.7	28	17.4	21	15.6	27.1	15.5	19.5	19.3	-	15	20.6
Properties at 40°C												
% Stress Relax., 160% extension for 30 min.	33.2	48.5	30.8	33.4	36	B	30.1	32.4	B	B	23.5	35.2

Note: ">" symbol indicates sample did not break at that elongation. A, B denotes samples failed prematurely during the test.

WE CLAIM:

1. An elastomeric film and fiber grade thermoplastic elastomer composition
5 comprising
 - (a) a block copolymer having at least two polystyrene endblocks and a midblock of hydrogenated polymerized butadiene which has a vinyl content of at least 60 percent by weight, a number average molecular weight of 40,000 to 110,000 and a styrene block number average molecular weight of 5,000 to 15,000;
 - 10 (b) optionally a tackifying resin;
 - (c) optionally a low molecular weight polyolefin; and
 - (d) optionally a polyolefin made with a metallocene catalyst having a density of 0.86 to 0.91, a molecular weight distribution of less than 3, and from 8 percent to 30 percent by weight of an α -olefin comonomer having from 4 to 12
15 carbon atoms;wherein the composition comprises either:
 - (i) from 60 to 85 percent by weight of component (a), from 5 to 30 percent by weight of component (b), and from 10 to 35 percent by weight of component (c); or
 - 20 (ii) from 65 to 95 percent by weight of component (a) and from 5 to 35 percent by weight of component (c); or
 - (iii) from 40 to 98 percent by weight of component (a) and from 2 to 60 percent by weight of component (d).
- 25 2. The composition of claim 1 where the block copolymer is a hydrogenated styrene-butadiene-styrene triblock copolymer with a polystyrene content of 12 to 25%.
3. The composition of claim 1 where the block copolymer is a hydrogenated
30 styrene-butadiene-styrene triblock copolymer with a number average molecular weight of 60,000 to 100,000.
4. The composition of claim 1 where the tackifying resin is a fully hydrogenated hydrocarbon resin.

5. The composition of claim 1 where the low molecular weight polyolefin is a low density polyethylene with a density of less than 0.92 grams per cubic centimeter and a melt index greater than 30 grams/10 minutes.
- 5
6. The composition of claim 1 wherein the vinyl content of the block copolymer is from 60 to 85 percent by weight.
7. The composition of claim 1 wherein the midblock of the block copolymer
- 10 further comprises hydrogenated isoprene or wherein the block copolymer is blended with another block copolymer comprising hydrogenated isoprene.
8. Elastomeric fibers or films from the extruded composition of claim 1.
- 15

INTERNATIONAL SEARCH REPORT

Internat Application No

PCT/US 01/31134

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08L53/02 C08F297/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08L C09D C09J C08F C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 709 413 A (JAPAN SYNTHETIC RUBBER CO LTD) 1 May 1996 (1996-05-01) * page 3, line 1-4 ; page 3, line 21-23 ; page 5, line 45-46 ; page 5, line 27-28 ; page 6, line 26-36 ; page 6, line 55-58 ; page 7, line 22-25 ; page 9, line 11-20 ; claim 11 * page 8, line 55 -page 9, line 3 ---	1-8
X	US 5 346 964 A (SHIBATA TOORU ET AL) 13 September 1994 (1994-09-13) * column 2, line 58-62 ; column 3, line 45-50 ; column 7, line 27-30 ; column 7, line 44-59, 64-66 ; column 10, line 3-10 ; column 10, line 51-58 ; column 13, line 39-54 * column 14, line 1-8; claim 1 --- -/-	1-8

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

1 February 2002

Date of mailing of the international search report

11/02/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Hammond, A

INTERNATIONAL SEARCH REPORT

Intern I Application No

PCT/US 01/31134

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 863 193 A (SHELL INT RESEARCH) 9 September 1998 (1998-09-09) * claims 1-8 ; page 6, line 1-6 ; page 2, line 1-6, 11-15, 29-35 ; page 4, line 29-34 ; page 4, line 41 - page 5, line 15 ; examples * -----	1-8
X	EP 0 822 227 A (SHELL INT RESEARCH) 4 February 1998 (1998-02-04) * page 2, line 46-58 ; page 3, line 6-10 * page 4, line 28-49; claims 5-8 -----	1-6
A	US 5 093 422 A (HIMES GLENN R) . 3 March 1992 (1992-03-03) cited in the application abstract; claims 1-4 -----	1-8
A	US 4 789 699 A (KIEFFER JOHN S ET AL) 6 December 1988 (1988-12-06) cited in the application abstract; claims 1-36 -----	1-8
P,A	WO 01 19919 A (SHELL INT RESEARCH) 22 March 2001 (2001-03-22) abstract; claims 1-5 -----	1-8

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern: Application No

PCT/US 01/31134

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0709413	A	01-05-1996	JP 2305814 A	19-12-1990
			JP 2754723 B2	20-05-1998
			EP 0709413 A1	01-05-1996
			DE 69032963 D1	08-04-1999
			DE 69032963 T2	19-08-1999
			DE 69033210 D1	19-08-1999
			DE 69033210 T2	09-12-1999
			EP 0398758 A2	22-11-1990
			US 5346964 A	13-09-1994
			US 5191024 A	02-03-1993
			US 5306779 A	26-04-1994
			JP 2764746 B2	11-06-1998
			JP 3072512 A	27-03-1991
			JP 3127872 B2	29-01-2001
			JP 10182925 A	07-07-1998
			JP 3128760 B2	29-01-2001
			JP 10182926 A	07-07-1998
US 5346964	A	13-09-1994	JP 2305814 A	19-12-1990
			JP 2754723 B2	20-05-1998
			US 5306779 A	26-04-1994
			DE 69032963 D1	08-04-1999
			DE 69032963 T2	19-08-1999
			DE 69033210 D1	19-08-1999
			DE 69033210 T2	09-12-1999
			EP 0398758 A2	22-11-1990
			EP 0709413 A1	01-05-1996
			US 5191024 A	02-03-1993
			JP 2764746 B2	11-06-1998
			JP 3072512 A	27-03-1991
			JP 3127872 B2	29-01-2001
			JP 10182925 A	07-07-1998
			JP 3128760 B2	29-01-2001
			JP 10182926 A	07-07-1998
EP 0863193	A	09-09-1998	US 5777043 A	07-07-1998
			AU 699760 B2	17-12-1998
			AU 5641098 A	10-09-1998
			BR 9800829 A	05-10-1999
			CN 1195012 A	07-10-1998
			EP 0863193 A1	09-09-1998
			TR 9800375 A2	21-05-1999
			TW 428021 B	01-04-2001
EP 0822227	A	04-02-1998	BR 9705233 A	29-06-1999
			CA 2211944 A1	31-01-1998
			EP 0822227 A1	04-02-1998
			JP 10077382 A	24-03-1998
			TR 9700720 A2	21-02-1998
			TW 416971 B	01-01-2001
			US 5926707 A	20-07-1999
US 5093422	A	03-03-1992	US 5304599 A	19-04-1994
US 4789699	A	06-12-1988	AU 603833 B2	29-11-1990
			AU 7975387 A	21-04-1988
			CA 1328940 A1	26-04-1994
			CA 1334376 A1	14-02-1995

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern: I Application No

PCT/US 01/31134

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4789699	A	DE 3734963 A1	21-04-1988
		FR 2605327 A1	22-04-1988
		FR 2672298 A1	07-08-1992
		GB 2197874 A , B	02-06-1988
		IT 1211860 B	08-11-1989
		JP 2853744 B2	03-02-1999
		JP 63178159 A	22-07-1988
		KR 9609298 B1	18-07-1996
		SE 468989 B	26-04-1993
		SE 8704015 A	16-04-1988
WO 0119919	A	AU 7656900 A	17-04-2001
		WO 0119919 A1	22-03-2001

THIS PAGE BLANK (USPTO)

THIS PAGE BLANK (USPTO)